ARKIV FÖR FYSIK Band 15 nr 38

Communicated 14 January 1959 by ERIK HULTHÉN

Rotational analysis of the $A\,^1\Pi - X\,^1\Sigma$ system of SnO

By ALBIN LAGERQVIST, N. E. LENNART NILSSON and KURT WIGARTZ

With 2 figures in the text

ABSTRACT

Rotational analyses of the 1,0, 0,0 and 0,1 bands of the A–X system of SnO have been carried out. The system corresponds to a $^1\Pi - {}^1\Sigma^+$ transition. Rotational constants for the upper and lower states have been derived. For the most abundant isotopic molecule $Sn^{120}O^{16}$ they are as follows:

$B_v' = 0.3145_5 - 0.0025\ (v' + \frac{1}{2})$ cm^{-1}; $r_e' = 1.950$ Å

$D_v' = [0.39 + 0.02 \times v'] \times 10^{-6}$ cm^{-1};

$B_v'' = 0.3561 - 0{,}0022\ (v'' + \frac{1}{2})$ cm^{-1}; $r_e'' = 1.832$ Å

$D_v'' = 0.29 \times 10^{-6}$ cm^{-1};

$\nu_e = 29624$ cm^{-1}.

Several perturbations have been found in the upper vibrational levels. One of the perturbing states is probably a $^1\Pi$ state.

Lines of the molecules $Sn^{118}O^{16}$ and $Sn^{116}O^{16}$ in the 0,1 band have also been measured. The shifts give $\varrho_{118}^2 = 0.99802$ and $\varrho_{116}^2 = 0.99594$.

Introduction

Several band systems lying in the blue and ultraviolet regions of the spectrum have been attributed to SnO. The system with $\nu_0 = 29503$ cm^{-1}, sometimes called A–X, sometimes D–X—here A–X—is the most prominent system. Early observations are given in the atlas of Eder and Valenta (1911). In 1931 Mahanti investigated the bands excited in an arc in air and arranged them into three systems. Connelly (1933) used a high tension arc passing through a hydrogen flame fed with $SnCl_4$, and gave a vibrational analysis for the A–X system from emission as well as from absorption measurements. He found in particular that the level $v' = 3$ is perturbed. Loomis and Watson (1934) investigated the ultraviolet E–X system in a tin arc, operated in oxygen at reduced pressure. Mahanti and Sen Gupta (1938) performed rotational analyses on the 1,0, 0,0 and 0,1 bands of the A–X system. They assumed that the system corresponds to a $^1\Sigma - {}^1\Sigma$ transition. In 1939 the same authors discussed the isotope lines in the 0,1 band. Eisler and Barrow (1949) extended the vibrational analysis of the E–X system from absorption exposures. The absorption spectrum in the Schumann region was measured by Barrow and Rowlinson (1954).

At a first glance Mahanti and Sen Gupta's rotational analysis seems to be very plausible. The B values are of the expected order of magnitude. It is peculiar, however, that the prominent singlet system in SnO should be $^1\Sigma$–$^1\Sigma$, whereas the corresponding system for all the related molecules CO, CS, SiO and SiS is a $^1\Pi$–$^1\Sigma$ transition. A thorough study of the reported combination differences shows that these agree very poorly. Accordingly we considered it desirable to carry out a new rotational analysis of this system.

Experimental

Different light sources for producing the SnO bands were tested, among others a high frequency discharge through a silica tube with $SnCl_4$ and streaming oxygen. The most intense light source, however, was found to be an arc in reduced oxygen between copper electrodes, of which the lowest one was furnished with a hole containing tin. The spectrograms were taken in both first and second orders of a 21 ft Wood grating with 165 000 lines. Several exposures with different exposure times (7 to 12 hours) on Ilford Thin Film Half Tone plates were made.

Analysis

Structure of the bands

Owing to rotational perturbations and to the great number of tin isotopes the analysis is rather difficult. The analyses, however, show unambiguously the presence of three branches, R, P and Q. Thus the transition must be $^1\Pi$–$^1\Sigma$. A reproduction of a part of the 0,1 band is given in Fig. 1*a*. The R, P and Q lines belonging to the most abundant molecules with Sn^{120}, Sn^{118} and Sn^{116} are marked. The figure shows clearly that the Q lines of $Sn^{120}O$ are more intense than all other lines not overlapped. Fig. 1*b* shows the part of the 1,0 band, where the vibrational and rotational isotope shifts cancel. The Q and R lines overlap each other for several J values, while the P lines are free. To the right the Q and R lines begin to separate more and more; the appearance of the spectrum in this short region suggests simple $^1\Sigma$–$^1\Pi$ structure without isotope lines. To the left the P lines are not numbered: there is a strong perturbation here which could not be studied in detail. It is remarkable that Mahanti and Sen Gupta made no mention of the perturbations in the upper vibrational states.

The 1,0, 0,0 and 0,1 bands have been analysed. The wave numbers for lines belonging to the most abundant isotopic species $Sn^{120}O^{16}$ are given in Table 1. For the 0,1 band the Q lines of $Sn^{118}O^{16}$ and $Sn^{116}O^{16}$ are also given.

Rotational and vibrational constants

The rotational constants were determined from the second differences $\Delta_2 F''(J) = R(J-1) - P(J+1)$ and $\Delta_2 F'(J) = R(J) - P(J)$. The constants derived are:

$B_1' = 0.3108$ cm^{-1}; $D_1' = 0.41 \times 10^{-6}$ cm^{-1}
$B_0' = 0.3133$; $D_0' = 0.39 \times 10^{-6}$
$\alpha' = 0.0025$
$B_1'' = 0.3527$ cm^{-1}; $D_1'' = 0.29 \times 10^{-6}$ cm^{-1}
$B_0'' = 0.3550$; $D_0'' = 0.29 \times 10^{-6}$
$\alpha'' = 0.0022$

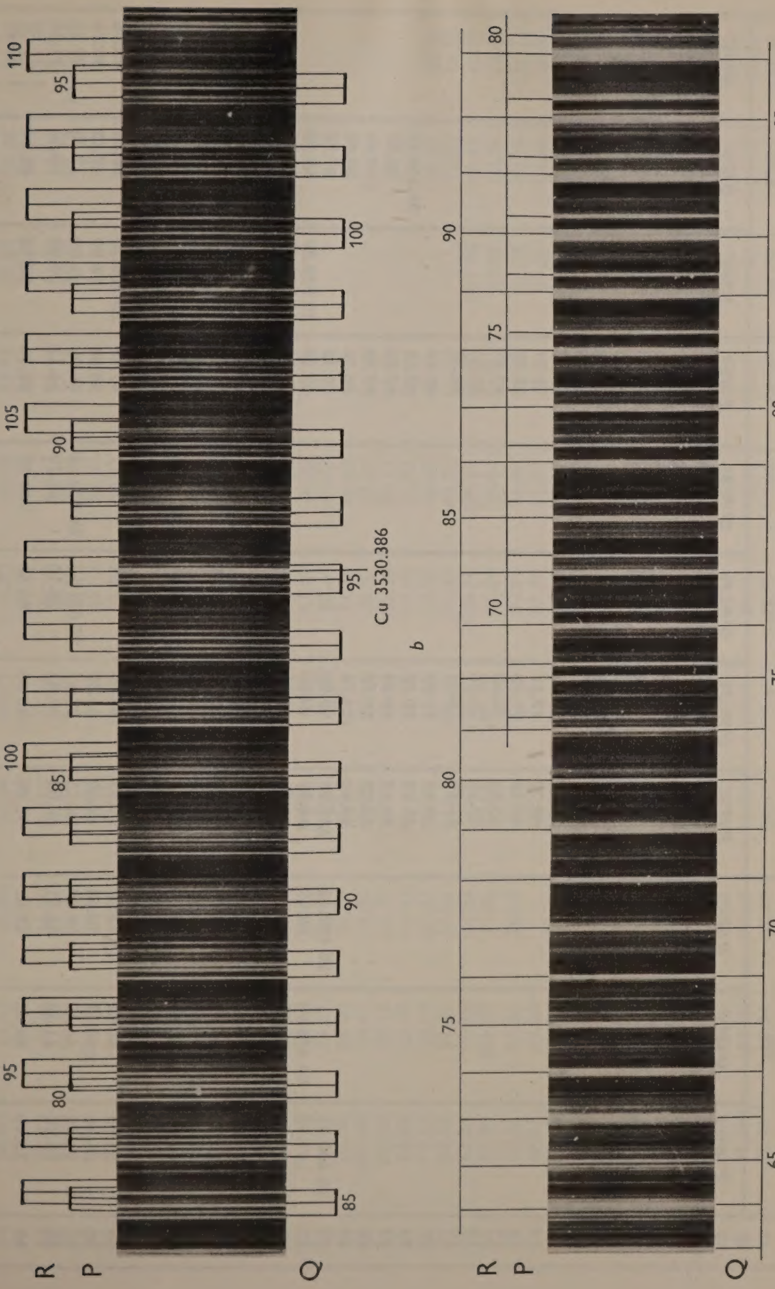

Fig. 1. Reproductions of parts of (*a*) the 0,1 band and (*b*) the 1,0 band. For the 0,1 band lines of the three main isotopes Sn^{120}, Sn^{118} and Sn^{116} are marked.

Table 1. Wave numbers for the 0,0, 0,1 and 1,0 bands.

J	0,0			0,1					1,0		
	$P(J)$	$Q(J)$	$R(J)$	$P(J)$	$Q^{120}(J)$	$Q^{118}(J)$	$Q^{116}(J)$	$R(J)$	$P(J)$	$Q(J)$	$R(J)$
9					28 685.10						
10					84.23			28 691.38			
11					83.22			90.95			
12					82.43			90.59			
13				28 673.23	81.45			90.19			
14				71.54	80.34			89.74			
15				69.73	79.12			89.21			
16				67.78	77.76			88.59			
17				65.82	76.50			87.83			
18				63.85	75.05			86.95			
19				61.86	73.61			86.06			
20				59.44	71.98			85.10			
21				57.12	70.29			84.11		30 056.17	
22				54.82	68.58			82.92		54.34	
23				52.27	66.73			81.65		52.26	
24				49.80	64.75			80.56		50.07	
25	29 460.67		29 492.44	47.08	62.96			79.12		47.78	
26	57.82	29 474.08	90.89	44.72	60.80			77.76	30 029.30	45.53	
27	54.95	71.73	89.14	41.79	58.75			76.18	26.29	43.13	
28	51.88	69.34	87.50	38.99	56.46			74.58	23.22	40.59	
29	48.83	66.82	85.63	35.95	54.13			72.90	20.03	37.97	
30	45.75	64.41	83.90	32.88	51.76			71.10	16.62	35.29	30 054.34
31	42.51	61.70	81.84	29.83	49.33			69.31	13.24	32.55	52.26
32	39.04	59.11	79.90	26.73	46.75			67.36	09.86	29.69	50.07
33	35.82	56.42	77.63	23.49	44.15			65.39	06.21	26.70	47.78
34	32.14	53.56	75.30	20.19	41.46			63.36	02.54	23.59	
35	28.72	50.61	73.03	16.87	38.64			61.19	29 998.76	20.36	42.74
36	24.96	47.51	70.68	13.50	35.83			58.84	94.90	17.12	40.15
37	21.20	44.47	68.89	09.75	32.87	28 631.94	28 630.88	56.59	91.00	13.93	37.43
38	17.29	41.16	65.91	06.03	29.83	28.79	27.79	54.13	86.96	10.50	34.55
39	13.49	38.03	63.02	02.36	26.73	25.66	24.57	51.76	82.75	06.90	31.28 32.55
40	09.74	34.69	60.18	598.50	23.49	22.51	21.40	49.13	78.62	03.10 04.13	27.10 28.84

45	88.50	16.65	45.25	78.31	06.38	05.29	04.17	35.02	56.15	83.92	12.33
46	84.06	12.65	42.03	74.04	02.71	01.63	00.50	31.81	51.37	79.73	08.75
47	79.46	08.75	38.61	69.64	598.92	597.85	596.78	28.79	46.42	75.41	05.02
48	74.78	04.69	35.20	65.18	95.06	93.96	92.87	25.51	41.38	71.04	01.24
49	69.99	00.57	31.76	60.65	91.16	90.05	88.84	22.36	36.38	66.49	29 997.27
50	65.19	396.51	28.16	56.02	87.30	86.07	84.94	18.93	31.25	61.92	93.22
51	60.46	92.11	24.46	51.55	83.10	81.94	80.77	15.44	25.86	57.09	88.81
52	55.37	87.70	20.70	46.57	78.93	77.66	76.59	11.85	20.31	52.06	83.92
53	50.21	83.24	16.90	41.72	74.69	73.54	72.27	08.20	14.53	46.42	77.92
54	45.08	78.69	13.02	36.75	70.30	69.14	67.88	04.50	8.50	39.85	70.39
55	39.82	73.99	08.75	31.74	65.96	64.77	63.63	00.68		31.25	
56	34.39	69.25	04.69	26.66	61.46	60.26	59.10	596.78			
57	29.01	64.47	00.57	21.55	56.85	55.69	54.46	92.87			
58	23.49	59.52	396.08	16.13	52.18	51.01	49.79	88.84		28.02	
59	17.86	54.50	91.72	10.84	47.44	46.28	44.90	84.66		22.28	
60	12.15	49.40	87.21	05.39	42.59	41.40	40.13	80.38		16.52	
61	06.35	44.21	82.79	499.87	37.67	36.44	35.23	76.11		10.76	
62	00.60	38.96	78.24	94.22	32.64	31.42	30.21	71.77		04.94	
63	294.49	33.61	73.26	88.52	27.61	26.33	25.07	67.22		899.16	
64	88.50	28.14	68.39	82.78	22.44	21.20	20.14	62.68		93.09	
65	82.35	22.57	63.61	76.90	17.17	15.94	14.94	57.99		87.06	
66	76.15	17.00	58.44	70.95	11.81	10.58	09.30	53.29		80.95	22.28
67	69.76	11.27	53.31	64.91	06.39	05.12	03.79	48.40		74.84	16.52
68	63.33	05.44	48.04	58.83	00.87	499.58	498.27	43.47	827.06	68.46	10.76
69	56.80	299.52	42.51	52.56	495.22	93.96	92.62	38.31	19.86	62.05	04.94
70	50.25	93.45	36.73	46.19	89.52	88.24	86.90	32.64	12.76	55.59	899.16
71	43.37	87.38		39.70	83.67	82.39	81.07		05.54	48.94	93.09
72	35.83	81.01		32.63	77.63	76.40	75.11		798.23	42.33	87.06
73		74.02			70.95				90.86	35.59	80.95
74									83.44	28.79	74.84
75		65.14			62.70			08.54	75.91	21.84	68.46
76		57.14	04.41		55.19	53.92	52.56	02.39	68.29	14.86	62.05
77		50.25	298.05	00.94	48.47	47.25	46.19	496.43	60.66	07.79	55.59
78	195.44	43.37	92.02	394.03	41.99	40.60	39.30	90.56	52.87	00.52	48.94
79	87.93	36.47	85.76	86.82	35.40	34.00	32.63	84.62	45.18	793.43	42.33
80	80.15	29.49	79.46	79.52	28.82	27.40	25.97	78.69	36.98	86.08	35.59
81	72.58	22.52	72.93	72.20	22.16	20.73	19.26	72.57	29.12	78.72	28.79
82	64.91	15.44	66.46	64.88	15.40	13.97	12.54	66.45	21.14	71.09	21.84
83	57.05	08.25	59.90	57.50	08.61	07.14	05.61	60.26	12.89	63.46	14.86
84	49.26	00.99	53.26	49.95	01.68	00.19	398.67	53.92	04.59	55.83	07.66
85	41.36	193.62	46.55	42.36	394.71	393.29	91.73	47.56	696.22	48.16	00.35

J	0,0			0,1					1,0		
	$P(J)$	$Q(J)$	$R(J)$	$P(J)$	$Q^{120}(J)$	$Q^{118}(J)$	$Q^{116}(J)$	$R(J)$	$P(J)$	$Q(J)$	$R(J)$
86	33.24	86.22	39.59	34.68	87.66	86.15	84.59	41.13	87.71	40.17	792.93
87	25.15	78.72	32.74	26.96	80.49	78.97	77.36	34.54	79.19	32.17	85.57
88	16.97	71.07	25.80	19.15	73.28	71.72	70.10	27.87	70.46	23.86	78.18
89	08.60	63.37	18.77	11.30	65.95	64.37	62.77	21.14	61.74	15.92	70.53
90	00.38	55.56	11.33	03.19	58.57	56.94	55.29	14.35	52.89	07.64	62.94
91	091.84	47.64	04.11	295.09	51.04	49.44	47.79	07.44	43.90	699.25	55.10
92	83.14	39.67	196.66	86.94	43.47	41.86	40.23	00.48	34.87	90.77	47.48
93	74.57	31.62	88.96	78.69	35.76	34.15	32.46	393.29	25.64	82.34	39.27
94	65.72	23.43	81.61	70.35	27.99	26.34	24.58	86.15	16.59	73.55	31.19
95	56.92	15.16	73.96	61.97	20.12	18.46	16.79	78.88	07.01	64.70	23.00
96	48.01	06.83	66.17	53.44	12.18	10.52	08.81	71.50	597.59	55.90	14.71
97	38.99	098.32	58.22	44.76	04.14	02.41	00.65	64.02	88.14	46.93	06.25
98	29.83	89.82	50.28	36.05	296.00	294.24	292.49	56.53	78.44	37.85	697.68
99	20.57	81.27	42.14	27.27	87.75	86.05	84.34	48.89	68.73	28.68	89.15
100	11.29	72.42	34.09	18.34	79.52	77.76	75.97	41.15	58.89	19.37	80.38
101	02.00	63.65		09.36	71.06	69.38	67.68	33.36	49.02	09.99	71.55
102	28 992.36			00.24	62.61	60.84	59.02	25.40	38.62	00.48	62.52
103				191.21	54.01	52.23	50.37	17.45	28.53	590.78	52.89
104				81.91	45.35	43.56	41.71	09.26		80.41	44.71
105					36.58	34.75	32.87	01.04		71.71	35.42
106					27.74	25.85	23.96	292.80		61.70	26.06
107					18.70	16.95	14.97	84.34		51.69	16.59
108					09.69	07.80	05.93	75.97		41.56	07.01
109					00.57	198.66	196.67	67.37		31.26	597.08
110					191.30	89.41	87.38	58.69			87.27
111					81.91	80.00		49.97			77.27
112								41.15			67.13

Table 2. Perturbations.

v'	J'	Remarks	v'	J'	Remarks
0	51	weak	1	40.5	rather weak
0	74.5	strong	1	55	strong
0	121	rather weak	1	104	rather weak

From the first combination differences of the upper state levels $\Delta_1 F'(J)$ we obtain, for $v' = 0$ and 1,

$$B_d' - B_c' \approx 4 \times 10^{-6}\ \text{cm}^{-1}.$$

The ν_0 values were determined from the Q lines as follows:

$$\nu_0 = Q(J) - (B' - B'')J(J+1) + (D' - D'')J^2(J+1)^2.$$

Thus

$$\nu_{1,0} = 30\,076.8\ \text{cm}^1$$

$$\nu_{0,0} = 29\,503.2$$

$$\nu_{0,1} = 28\,688.6$$

From the differences $(\nu_{1,0} - \nu_{0,0})$ and $(\nu_{0,0} - \nu_{0,1})$ we obtain $\omega_e' - 2\omega_e' x_e' = 573.6$ and $\omega_e'' - 2\omega_e'' x_e'' = 814.6$. With Jevon's (1938) values $\omega_e' x' = 3.08$ and $\omega_e'' x_e'' = 3.73$ we get

$$\omega_e' \approx 580\ \text{cm}^{-1} \quad \text{and} \quad \omega_e'' = 822.1\ \text{cm}^{-1}.$$

Perturbations

Several perturbations have been found in the upper vibrational levels. At all perturbations detected both the R and P lines as well as the Q lines are shifted, and the culmination of interaction takes place at the same J value for the Q lines as for the R and P lines. This fact indicates that the perturbing states have $\Lambda \geqslant 1$. The appearance of the perturbations suggests singlet-singlet interactions. Thus the perturbing states are probably $^1\Pi$ or $^1\Delta$ states. In all, six perturbations have been found. The positions of the perturbations are given in Table 2.

The perturbation at $v' = 0$, $J' = 51$ is extremely weak and could not be found with certainty in the 0,0 band, which is more difficult to analyse than 0,1 due to the abundance of lines in the background. The perturbations at $v' = 0$, $J = 121$ have not been analysed but the Q lines can easily be observed on the plates and on photographic reproductions. It has not been possible to identify extra lines in the perturbed regions with certainty, although in the strong perturbation at $v' = 1$, $J = 55$ some extra lines—not given in the tables—fit very well. If these lines are the right ones, the B value of the perturbing state is 0.247 cm^{-1}.

Isotope effect

Tin has ten stable isotopes with the following masses and abundances:

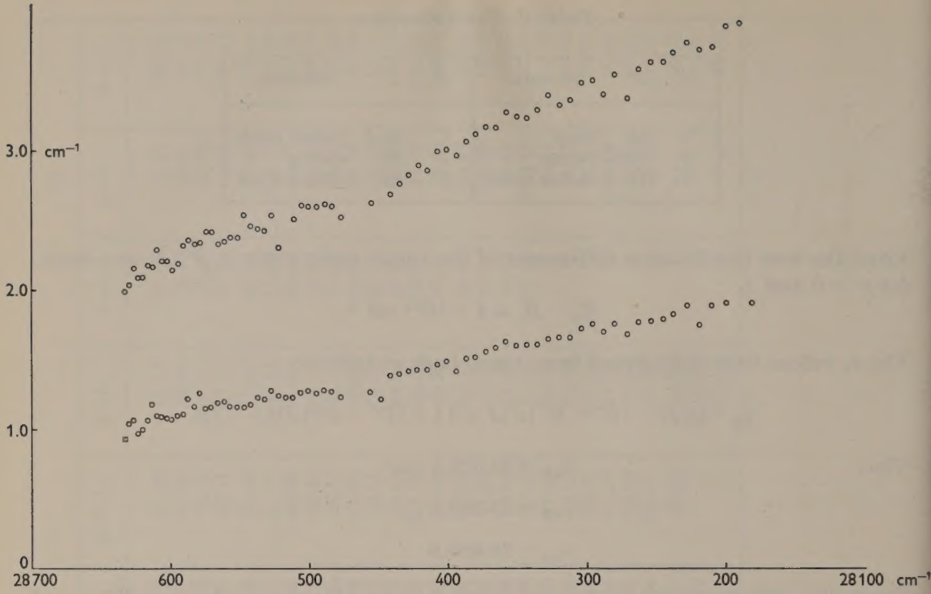

Fig. 2. Isotope shifts of Sn^{118} and Sn^{116} lines for the 0,1 band plotted against the wave numbers.

112	0.95 %	118	24.01 %
114	0.65	119	8.58
115	0.34	120	32.97
116	14.24	122	4.71
117	7.57	124	5.98

The three lightest isotopes are rare but the other seven all contribute to the spectrum. In our analysis we have not made any efforts to find all isotope lines. For the three investigated bands we have picked out the three most abundant isotopes 120, 118 and 116 in the Q branches. For the 0,1 band these isotope lines have also been analysed in the P and R branches. A part of the 0,1 band with these isotope lines is given in Fig. 1a. From considerations of space only the wave numbers for all the three isotope lines are given only for the Q branch in 0,1 in Table 1. The isotope shifts of $Sn^{116}O$ and $Sn^{118}O$ are plotted against the wave numbers of $Sn^{120}O$ in Fig. 2. From the slopes we get

$$\varrho_{118}^2 = 0.99802 \quad \text{and} \quad \varrho_{116}^2 = 0.99594.$$

From mass spectrometric determinations of the atom masses (see for example, Townes and Schawlow, 1955) one gets

$$\varrho_{118}^2 = 0.998007 \quad \text{and} \quad \varrho_{116}^2 = 0.9959547.$$

Mahanti and Sen Gupta (1939) investigated the isotope lines in the 0,1 band. Their task was, of course, impossible, as their rotational analysis was incorrect. Nevertheless

Table 3. The states $A\,^1\Pi$ and $X\,^1\Sigma^+$ of the molecules CO, SiO, SnO, CS and SiS.

State	Molecule ...	CO	SiO	SnO	CS	SiS
$^1\Pi$	ν_0	64746.5	$42640._4$	29503.2	38798	34908.5
	ω_Π	1515.61	852.7_1	579.7	1081.2_0	513.1_2
	ω_Π/ω_x	0.698	0.687	0.705	0.841	0.684
	B_Π	1.6116	0.6313	0.3146	0.7799_5	0.2664_7
	B_Π/B_x	0.835	0.868	0.883	0.951	0.888
$^1\Sigma^+$	ω_x	2170.21	1241.4_4	822.1	1285.08	749.69
	B_x	1.9313_9	0.7273	0.3561	0.82005	0.3036_3

they managed to find the isotope lines of Sn^{116}, Sn^{118}, Sn^{122} and Sn^{124}, but detected no trace of the isotopes Sn^{117} and Sn^{119}, which are more abundant than Sn^{122} and Sn^{124}.

Discussion

This rotational analysis establishes that the intense singlet-singlet system in SnO is a $^1\Pi$–$^1\Sigma$ transition, in agreement with the other spectra of diatomic molecules from the fourth and second periods (CO, CS, SiO, SiS). A comparison of the two states, $A\,^1\Pi$ and $X\,^1\Sigma^+$, for these five molecules is given in Table 3. The electronic configuration for the ground state of SnO gives a $^1\Sigma^+$ state exactly as for the other molecules here mentioned.

A rotational analysis of the corresponding system in GeO was given by Sen Gupta (1939) who assumed that the transition was a $^1\Sigma^+$–$^1\Sigma^+$. The combination differences, however, agree here as poorly as in the rotational analysis of SnO by Mahanti and Sen Gupta. It seems very probable that this analysis also is incorrect and that this system too corresponds to a $^1\Pi$–$^1\Sigma$ transition.

The ground state of oxygen is a ^3P state. the ground states of C, Si and Sn are also ^3P states. The ground states of the molecules CO, CS, SiO, SiS and SnO dissociate into the ground states of the atoms. For the four molecules CO, CS, SiO and SiS the $A\,^1\Pi$ state also dissociates into the normal states of the atoms. It seems to us that this is also the case with $A\,^1\Pi$ in SnO. Some years ago (1954) this statement was maintained also by Barrow and Rowlinson. For the ground state $X\,^1\Sigma^+$ in SnO a linear Birger–Sponer extrapolation for the dissociation energy gives $D_e = 45\,000$ cm^{-1}. This value agrees well with values for D_e obtained through thermochemical data (Brewer, 1953; Barrow and Rowlinson, 1954.)

Connelly showed the existence of vibrational perturbations in the $A\,^1\Pi$ level. The perturbations are rather strong—up to 40 cm^{-1}—so that the values for the vibrational constants are difficult to derive. Jevons (1938) recalculated these constants from Connelly's measurements. With Jevon's values the dissociation energy for $A\,^1\Pi$ is about 11 000 cm^{-1}. As ν_e for $A\,^1\Pi$ is about 30 000 cm^{-1} these data correspond to a dissociation energy for the ground state of 41 000 cm^{-1}, which indicates that the vibrational constants by Jevons are slightly incorrect. In any case from the calculations made above it seems most probable that $A\,^1\Pi$ dissociates into the normal state ^3P(Sn) and ^3P(O) of the atoms. The nearest atom pair, which can give birth to a $^1\Pi$ state, is $^1D(\mathrm{Sn}) + {}^1D(\mathrm{O})$ which lies more than 20 000^{-1} above the combination $^3P + {}^3P$.

Physics Department, University of Stockholm, January 1959.

REFERENCES

BARROW, R. F., and ROWLINSON, H. C., 1954, Proc. Roy. Soc. *224 A*, 374.
BREWER, L., 1953, Chem. Rev. *52*, 1.
CONELLY, F. C., 1933, Proc. Phys. Soc. *45*, 780.
EDER, J. M., and VALENTA, E., 1911, Atlas typischer Spektren.
EISLER, B., and BARROW, R. F., 1949, Proc. Phys. Soc. *62 A*, 740.
JEVONS, W., 1938, Proc. Phys. Soc. *50*, 910.
LOOMIS, F. W., and WATSON, T. F., 1934, Phys. Rev. *45*, 805.
MAHANTI, P. C., 1931, Z. Physik *68*, 114.
MAHANTI, P. C., and SEN GUPTA, A. K., 1938, Z. Physik *109*, 39.
—— 1939, Ind. J. Phys. *13*, 331.
SEN GUPTA, A. K., 1939, Proc. Phys. Soc. *51*, 62.
TOWNES, C. H., and SCHAWLOW, A. L., 1955, Microwave Spectroscopy. McGraw-Hill, New York.

Tryckt den 14 maj 1959

Uppsala 1959. Almqvist & Wiksells Boktryckeri AB